Chemical modifications and applications of alternating aliphatic polyketones

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Chapter 1

Introduction

Abstract

A general overview on historical development, synthesis, catalysis, properties, applications, and chemical modifications of polyketones is provided. In particular, applications of polyketones as such and their deviratives obtained after chemical modifications are discussed. Chemical product engineering, an emerging paradigm within the chemical engineering sciences, is introduced and the framework of chemical product design is discussed. Finally, the aim and scope of this thesis is presented.

1.1 Historical overview of aliphatic polyketones

Aliphatic polyketones, a new family of polymers, are produced by copolymerization of carbon monoxide (CO) and various unsaturated hydrocarbon monomers (e.g. olefins). When compared to the corresponding polyolefins, these polyketones have the following advantages: (i) CO as monomer is a particularly low-cost feedstock; (ii) the polymers can act as excellent precursors for the preparation of functional polymers by chemical modifications using the recurring highly reactive 1,4-di-carbonyl functionality; (iii) the reactive carbonyl groups in the backbone confer photo- and biodegradability; (iv) they can be used for a variety of applications due to their unique physical and chemical properties.

The first copolymerization of CO and ethylene, leading to random aliphatic polyketones, was discovered in 1941 by the researchers of Farbenfabriken Bayer using extreme conditions (230 °C, 2000 atm).[1] One decade later, alternating aliphatic polyketones were reported by Reppe and Magin using a nickel-based catalyst in water under relatively mild conditions (200 °C, 200 atm).[2] Since then, considerable efforts have been made by both academia and industry towards the development of new and industrially viable catalytic systems. However, only in the 1980s, a technological breakthrough was achieved by Shell researchers with the development of a highly efficient homogeneous palladium-based catalytic system.[3-6] This catalyst, a palladium (II) complex bearing bidentate phosphine or nitrogen ligands with a Brønsted acid as co-catalyst, enabled the production of high molecular weight, perfectly alternating copolymers of carbon monoxide and olefins. This catalytic system can also be applied to mixtures of olefins, which in turn can be simple aliphatic or heteroatom functionalized ones. Production yields that satisfied the economic requirements for industrial production were achieved, i.e. 6 (kg of polymer) (g of Pd)$^{-1}$h^{-1}, under mild conditions (90 °C, 4-5 MPa).

Following the discovery of these catalyst systems, alternating polyketones have attracted considerable interest from both academia and industry.[7-15] The polymerization mechanisms to achieve alternating polyketones have been determined by Sen *et al.*[8] and Drent *et al.*[9]. In 1996, after nearly 20 years of intensive research, Shell introduced a number of CO/ethylene/propylene-based terpolymers, a class of engineering thermoplastics, in the plastics market under the trademark of Carilon.[16] However, Shell withdrew the business of Carilon Polymers from the market in 2001 because of a strategy change in their chemical business. Nevertheless, research on catalyst improvements and polyketone application development continued in academia. Particularly interesting is the preparation of functionalized polyketone derivatives, which may open many new applications in different research fields (e.g. material and biomedical sciences) as demonstrated in the present thesis.

1.2 Properties and applications of alternating aliphatic polyketones

Alternating polyketones (Figure 1.1) are produced by the copolymerization of CO and alkenes, dienes, styrene and its derivatives, using catalysts based on transition metal compounds. The obtained polymers range from amorphous liquids of low molecular weight (thermosets) to crystalline solids of high molecular weight (thermoplastics). The molecular weight depends on the reaction conditions, the type of olefins, and the type of catalyst.

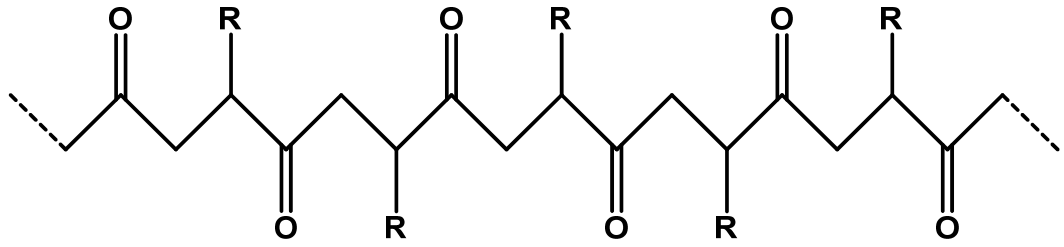

Figure 1.1 Scheme of perfectly alternating polyketones (R=H, CH_3, C_6H_5, etc.).

Most of the product and research & development is focused on the synthesis of aliphatic copolymers of CO with ethylene, propylene or mixtures of olefins.[9] High molecular weight copolymers of ethylene and CO, in a perfectly 1:1 alternating order, represent the simplest members of the family of alternating aliphatic polyketones. Their alternating chemical structure has been thoroughly studied and confirmed by elemental analysis, nuclear magnetic resonance (NMR), and FTIR spectroscopy.[17-19] These polymers are semi-crystalline thermoplastics with levels of crystallinity in the range of 35-50%.[10] Two different crystalline structures (α and β form) in an all-trans configuration have been detected by X-Ray diffraction.[20-23] Semicrystalline polyketones are insoluble in common organic solvents and only dissolve in highly polar and acidic solvents (e.g. hexafluoroisopropanol, *m*-cresol). The strong interaction between polymer chains and the high stereo-regularity of the ethylene-CO polymers lead to highly crystalline materials with a relatively high melting point (T_m, typically between 250 °C and 260 °C). However, this high melting range of CO-ethylene copolymers is close to the thermal decomposition temperature which makes their melt processing very difficult. In addition to thermal degradation, the high reactivity of the 1,4-di-carbonyl moiety often results in condensation reactions, leading to the formation of furan structures at elevated temperatures. As a result, ethylene/CO copolymers have limited practical use in the applications that require the melt-processing of the polymers.

Terpolymers of CO, ethylene and propylene show a reduced T_m due to the incorporation of a certain amount of propylene/CO segments into the polymer backbone.[19] The melting point of the terpolymers is dependent on the number of propylene units in the polymer

backbone. For instance, the incorporation of 6% and 17% propylene leads to a melting point depression till 220 °C and 170 °C, respectively. The terpolymers possess excellent properties like fast crystallization rate, better mechanical properties in comparison to other thermoplastics (e.g. polyamide-6, polypropylene, low and high density polyethylene), high chemical resistance to a broad range of chemicals, and good barrier properties to gases (e.g. oxygen) and hydrocarbon fuels.[24-25] These properties enable aliphatic polyketones to be used in a variety of applications: as fibers[26-33], in polymer blends[34-43] and polymer composites[44-52], in packaging materials[53-60], as flame resistant materials[61-65], etc.

Another class of alternating aliphatic polyketones is represented by thermosetting polyketone oligomers (the main focus of this thesis) produced by the co- and ter-polymerization of CO, ethylene, and proplyene.[66-68] Like high molecular weight polyketones, thermosetting oligomers are synthesized in an organic solvent using a homogeneous palladium-based catalyst at a reaction temperature of 70–100 °C and a pressure of typically up to 8.5 MPa. The product composition is a function of the molar ratio between propylene and ethylene in the oligomers, ranging from viscous resins for the ethylene-free types to waxy or melting solids at ethylene contents of about 50% based on total olefin content. Because of the presence of highly active carbonyl groups, chemical conversion of thermosetting polyketones can be carried out in a variety of ways (e.g. condensation to polyfurans, reduction to poly-alcohol, and condensation with commercial formaldehyde resins).[69] The Paal-Knorr reaction, involving pyrrole ring formation between an amino group and two adjacent carbonyl groups, has been used as a powerful cross-linking tool for these materials (Figure 1.2). In this curing reaction, aromatic pyrrole units are formed through the elimination of water, using a variety of di- or multi-functional amino-based curing agents familiar to the epoxy-resin technology. Product and application development of these thermosetting resins mainly focused on coating[70-71], wood adhesives[72-75], electronic adhesives[76-78], and polymer composites, which are thermosetting areas dominated by commercial resins like epoxy, urea-formaldehyde or phenol-formaldehyde. All these applications require relatively fast cure chemistry, easy handling, and the absence or control over volatile and toxic components.

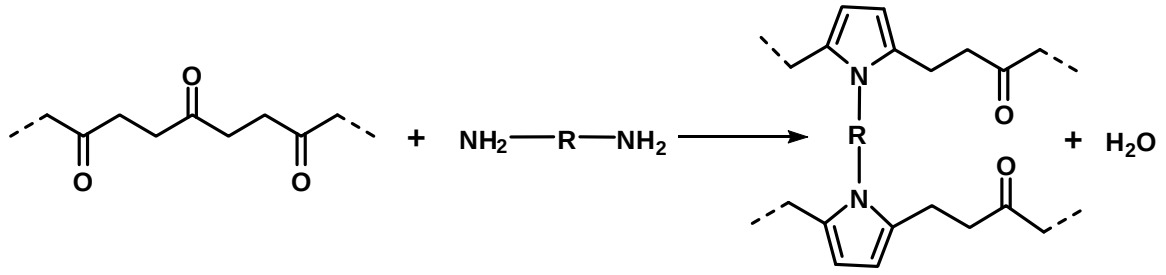

Figure 1.2 Paal-Knorr curing chemistry for thermosetting polyketones.

1.3 Functional polymers from alternating polyketones

Functional polymers are by definition those that bear specified chemical groups or have specified physical, chemical, biological, pharmacological applications which in turn depend on the presence of specific chemical groups.[79] The functional groups could be part of the polymer backbone or be linked to the main chain as pendant groups (either directly or via a spacer group). Functional polymers have found numerous applications like organic electronics, chemical sensors, medical devices, artificial organs, fuel cells, and nano devices, etc., in a great variety of areas.[80-88] Direct polymerization of functional monomers (e.g. anionic, cationic, radical, and metal catalyzed polymerization) and chemical modification of synthetic polymers are considered as the two general routes for the preparation of functional polymers.[89] Each of the two approaches has its own advantages and disadvantages. One approach may be suitable for the preparation of a particular functional polymer whereas the other would be totally impractical. In general, the polymerization route can lead to polymers with a homogeneous and uniform structure (e.g. distribution of the functional groups within a single chain and between different chains), while the use of chemical modification enables the creation of new classes of polymers which are difficult to synthesize by direct polymerization of the monomers. The design simplicity and the ease of synthesis are the accepted main features of the chemical modification route. The choice between the two different approaches is mainly dependent on the required chemical and physical properties of the polymers and the feasibility of the desired chemistry.

Alternating polyketones constitute a very interesting class of polymers as they can be applied as starting materials for the preparation of functional polymers by chemical modifications. As these polymers contain the highly reactive 1,4-di-carbonyl functionality, the systems can readily be converted into a great variety of polymers containing functional groups such as pyrroles[90], furans[91], thiophenes[91], bisphenols[92], alcohols[93-94], ketals[95-96], thiols[97], oximes[98-99], methylene[100], cyanohydrins[101], etc., via different reaction pathways (Figure 1.3). Among these modifications, the classic Paal-Knorr reaction, in which the 1,4-di-carbonyl moiety of the polyketones reacts with a primary amine function yielding a pyrrole unit, is one of the dominating reaction routes for the functionalization of alternating polyketones.[74,102-106] The obtained poly-pyrrole derivatives exhibit good solubility in common organic solvents. The pyrrole function is also one of the most important heterocycles and the key unit in many biologically active compounds and synthetic pharmaceuticals.[107] The Paal-Knorr reaction can be carried out under mild experimental conditions without the need for any catalysts and solvent. Particularly interesting is the preparation of polymeric amines via this type of reaction[74], which has been main focus

study in this thesis. Polymers containing amino functionality (e.g. primary, secondary, and tertiary amines) have found wide applications in various areas, such as chelating agents for metal ion[108], polymeric surfactants[109], polyelectrolytes[110], ion exchange resin[111], DNA carriers for gene delivery[112], polymeric pharmaceuticals[113], and antibacterial and bacterium adsorbing polymers[114].

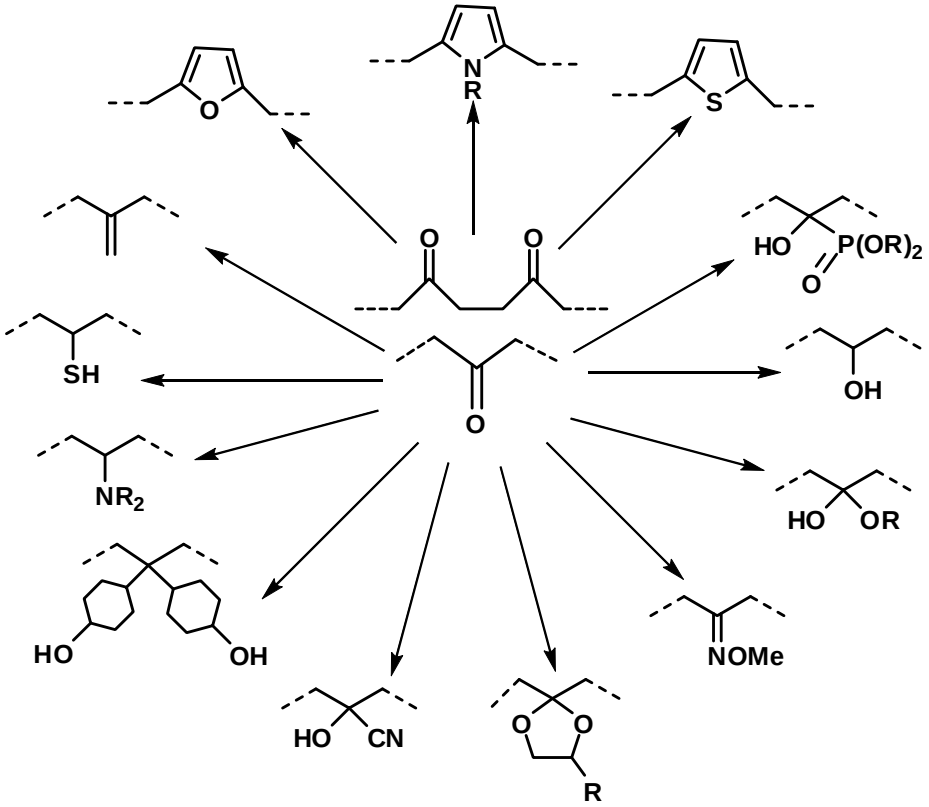

Figure 1.3 Scheme of chemical modifications of polyketones.

1.4 Chemical product engineering

Chemical Engineering is by definition the branch of engineering that deals with the application of natural sciences (e.g. chemistry and physics) with mathematics to the process of converting raw materials or chemicals into more useful or valuable forms.[115] However, the activities of chemical industries during the last few decades have been undergoing dramatic changes: from commodity chemicals (large quantity, low value added) to specialty chemicals (small quantity, high value-added, e.g. pharmaceuticals, functional polymers) and to even more sophisticated structured chemical products (e.g. paints, personal care or household products, biomedical devices, and semiconductors).[116-118] To address the current industrial demands, chemical engineering sciences have been reacting to this shift in industrial development.[119,120] As one of the main results, Chemical Product Design and Engineering (CPDE) is becoming a well-established branch of Chemical Engineering.[119-126] It can be defined as the discipline which combines science

and technology for the development and production of structured chemical products able to meet the demands and requirements of society. This is usually achieved by improving existing products and designing new ones.[124] This goal and the corresponding research methodology combine market pulls with technological pushes to arrive at unique products.[119,120] A new conceptual model or structure for this new discipline (CPDE) has also been proposed by Moggridge *et al.*,[126] in which three fundamental inter-related pillars were suggested to support the major objective of designing new chemical products: (i) the chemical product pyramid, i.e. the combination of usage functions, process, and property in the design of a chemical product; (ii) the integration of chemical product and process design; (iii) a multifaceted approach considering product design at different dimensional levels.

Chemical product design (CPD), considered as the core part of CPDE, is defined as a systemic procedure or framework of methodologies and tools, whose aim is to provide a more efficient and faster design of chemical products able to meet market needs.[126] CPD has recently been introduced into the Chemical Engineering curriculum at a number of universities because of its well-accepted importance.[121,126-129] CPD, according to Cussler *et al.*, mainly comprises four essential steps: (i) identification of customers needs; (ii) generation of product ideas; (iii) selection of the most promising ideas; (iv) development of a process to manufacture the products.[130-131] Other similar systematic frameworks about the design of chemical products have also been proposed through many detailed case studies of chemical-based products.[131-140] A toolbox of molecular structure-property relations, based on the maturity of current scientific understanding, has been developed by Wei[119,141] to design as well as manufacture new materials or products with desired properties. The available methods proposed by Wei include the use of additives and blending, addition and substitution of functional groups, isomerization and skeletal rearrangements, and the cross-linking of molecular chains. It should be pointed out that a multidisciplinary team is generally required for a successful product development due to the complexity of this concurrent process and product creation activity.

1.5 Aim and scope of this thesis

The aim of this thesis is to enhance the fundamental understanding regarding the development of new products and product applications by using aliphatic alternating polyketones based on low molecular weight ethylene/propylene/CO co- and terpolymers. The work has been carried out within several research disciplines and covers the full pathway from molecular design (i.e. chemical modifications of polyketones) to product development. New chemical products based on polyketones have been developed with good performance: (i) polymeric surfactants; (ii) water-borne formaldehyde-free wood

adhesives; (iii) thermally self-healing polymeric materials; (iv) polymeric interlinkers for carbon nanotubes; (v) new biomaterials for controlling cell behavior. The layout of this thesis is given below.

Chapter 2 focuses on chemical modifications of alternating polyketones by using a series of di-amines via the Paal-Knorr reaction to prepare polymeric amines (polyamines). The chemical reactivity of the polyketones with the di-amines and characterization of the obtained polyamines in water as polymeric surfactants have been studied.

Chapter 3 describes the preparation of wood adhesive emulsions. The stability and structure of the emulsions were thoroughly studied at different experimental conditions with respect to the storage time (up to 2 years) at room temperature. The performance of the wood adhesives was evaluated according to the European Standard (EN-314) for wood adhesive testing.

Chapter 4 describes a thermally self-healing polymer system on the basis of furan functionalized alternating olefin-CO polyketones and bismaleimide by using the Diels-Alder and Retro-Diels-Alder reaction scheme. The self-healing ability of this system has been studied by using several analytical and mechanical testing techniques, which prove excellent self-healing performance.

Chapter 5 reports an approach for the preparation of carbon nanotube interconnects by using polymeric amines to functionalize and cross-link multi-walled carbon nanotubes (MWNTs) via the amidation reaction. The obtained systems have been characterized using several analytical and microscopy techniques.

Chapter 6 describes the use of polymeric amines for biomedical applications. The response and behavior of vascular smooth muscle cells and bovine arterial endothelial cells upon exposure to the polyamine films and polyamine solutions were investigated *in vitro*.

1.6 References

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